



# Acid–base equilibrium in conducting polymers. The case of reduced polyaniline



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## ABSTRACT

The understanding of the acid–base properties of conducting polymers (CPs) is essential for a rational design of devices based on this type of materials. Much of the work about polyaniline protonation equilibrium is focused on the emeraldine form. However, for the complete description of the pH effect on the electrochemical behaviour, it is required the knowledge of proton binding equilibrium to both the reduced (leucoemeraldine) and the oxidized (emeraldine) forms. In this work, the acid–base titration of polyaniline films was performed by spectroelectrochemistry at constant applied potentials so to keep the polymer in its reduced form. The values of the apparent dissociation constant,  $pK_{a,app}$ , result to be about 1. The analysis of the proton binding degree as a function of pH allows determining the distribution of dissociation constants. This distribution is interpreted in terms of a simple thermodynamic statistical model, that allows determining the internal dissociation constant,  $pK_{a,int} \approx 1.3$ . Comparison with the  $pK_a$  values of related monomers reinforces the results obtained in this work.

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## 1. Introduction

One of the most important applications of Polyaniline (Pani) and its derivatives is as pH sensors of different types: potentiometric [1–5], conductimetric [6], amperometric [7], or based on its optical properties [8–10]. For this reason, the knowledge of the acid dissociation constant value, of the different redox forms of Pani, is a relevant subject.

Previously, it was shown that the electrochemically active macromolecules present coupling effects among the states of deformation, binding, and the redox potential [11–13]. Thus, the redox potential of Pani depends on the pH of the external medium through the Nernst equation (Fig. 1) but it also depends on the state of binding of the macromolecule. Electrochemically active polymers, being polyelectrolytic in nature, show these effects. It deserves to remark that, due to the coupling effects mentioned above, one characteristic of these polyelectrolytic materials is that they do not have a single value of the dissociation constant but a distribution of them [14–16]. This means that the dissociation constant is a function of the dissociation degree.

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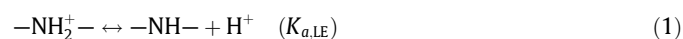
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Pani, in its reduced state (that is, the leucoemeraldine (LE) form), participates of a redox reaction to yield the emeraldine (E) form. This reaction can be represented as in Fig. S1.1 [17,18]. According to the pH of the external medium both of them will be protonated to a certain degree. Moreover, it deserves to remark that being the E form composed of amines and imines groups, these moieties will be protonated to a different degree, at the same pH. Then, it is interesting to have reliable values of the ionization constant of both forms, LE and E; noting that the amine groups, in the LE and E forms, might have different  $pK_a$  values. Moreover, being the E form the product of the chemical synthesis and the electronically conducting form, it has been more thoroughly studied. On the other hand, the LE form has received much less attention.

After Genies and Vieil [19], each protonated amine group of the LE acid form can be represented as  $-\text{NH}_2^+$ .

Then, the acid–base equilibrium of the LE form can be written as:



where  $K_{a,LE}$  is the acid dissociation constant of the protonated amine groups of the LE form.

In the case of the E form, its chemical structure can be depicted as an alternation of benzoid (amine) and quinoid (imine) rings. Alternatively, other structures with equivalent nitrogen atoms

can be written (Fig. SI 2). The acid base equilibrium of the imine groups in the E form can be written as [19]:



where  $K_{a,E}$  is the acid dissociation constant of the E form.

In Table 1, it is assembled the values of the dissociation constants reported by different authors for the equilibria represented by Eqs. (1) and (2), together with a brief description of the method employed. Far from being complete, this table summarizes two main aspects that are found in the literature of Pani acid–base equilibrium. The first one is the wide dispersion of  $\text{p}K_a$  values reported for the emeraldine state. This fact could be related to the synthesis conditions and the fact that the potential was not kept constant. Moreover, in polyelectrolytes there are other factors that also change the  $\text{p}K_a$  value [11,12,14–16,39]. In particular, for Pani films, it has been observed that the  $\text{p}K_a$  values depend on the polymer synthesis conditions, in different aspects such as the synthesis solution pH, the nature of the acid employed [32,34] and also, the way in which the electrosynthesis is performed (galvanostatic, potentiostatic, or potentiodynamic) [31].

Furthermore, there is scarce information about acid–base equilibrium of the leucoemeraldine form.

Some authors have considered that the  $\text{p}K_a$  values of both redox forms of Pani are not independent, but they are related by a redox internal equilibrium (bipolaron formation equilibrium) that depends on the oxidation degree [40]. Other authors recognize the existence of an acid dissociation constant distribution and interpret it in terms of fractional numbers of exchanged protons [31,32,34,35]. Also, theoretical models have been developed to take into account the dependence of the  $\text{p}K_a$  values on the dissociation degree, but they do not consider the effect of the oxidation degree [24,28].

On the other hand, it is useful to remember that the experimental procedure to perform the titration curves of Pani presents several intrinsic difficulties. If the polymerization is chemically performed, the titration of the Pani dispersion obtained will require long equilibration times [19,23]. This difficulty can be minimized employing thin Pani films and performing the titration spectrophotometrically. Another difficulty is related to the dependence of the apparent redox potential on the state of proton binding of the polymer [12,13]. So, the state of oxidation of the polymer will be liable to change during the titration unless the experiment is carried out at constant applied potential. The results summarized in Table 1, except those of Ref [22], have been obtained without potential control.

In a previous work, the  $\text{p}K_a$  values of the reduced form of Pani were determined in an indirect way, by employing the redox potential dependence on pH [13]. The values obtained, as compared with those reported in the literature, were surprisingly about

1. However, due to the lack of previous experimental information about the acid–base behaviour of the reduced form, an acid–base study of the leucoemeraldine form is needed for testing the validity of that model. So, in this work it is performed an experimental study of the acid–base equilibrium of the reduced form of Pani (LE), in electrolytic media of different pH at constant ionic strength. In order to explore the effect of the potential the experiments were carried out at three different applied potentials, all of them near the value of the complete polymer reduction. The experimental results, obtained by a spectrophotometric method at potential controlled conditions, are analyzed within a simple theoretical model in which the interactions between proton binding sites are considered.

## 2. Experimental

Pani films were electrosynthesized onto ITO (Indium Tin Oxide) plates ( $R_s = 5\text{--}15 \Omega \text{ cm}$ , Delta Technologies) from 0.5 M aniline in 3.7 M  $\text{H}_2\text{SO}_4$  solutions, as described elsewhere [13,41]. These plates were glued to a metallic contact with epoxy silver resin. The top and sides of the metallic plate were covered with an insulating varnish [13]. The active area of the polymer covered ITO was around  $1 \text{ cm}^2$ . Stability of ITO electrodes in all employed acid solutions was verified as its voltammetric response was constant even after several hours.

The Pani electrosynthesis was carried out by cycling the potential at  $0.1 \text{ V s}^{-1}$  between  $-0.2 \text{ V}$  vs. SCE and a positive potential limit set at the beginning of the monomer oxidation (around 0.7–0.8 V). All the films were built up to an approximate charge around  $Q = 32 \text{ mC cm}^{-2}$ . To improve the adherence and homogeneity of the film, after a few cycles, the positive potential limit was decreased to 0.65 V. At the end of the electrosynthesis, the film was washed with pure water, cycled in 3.7 M  $\text{H}_2\text{SO}_4$  during some minutes and then introduced in the spectrophotometrical cell. This was a square quartz cell (Spectrocell, 1 cm side) in which the electrode was inserted perpendicular to the light path [13]. A small Pt plate served as the counter electrode. The reference electrode was a Saturated Calomel Electrode (SCE) connected to the solution through a fine pointed capillary. In this work, all potentials are referred to the SCE. A potentiostat TEQ-02 was employed for all the electrochemical experiments.

Spectra were taken with an Agilent model 8453E diode array spectrophotometer in the spectral range comprised between 300 nm and 900 nm. Electrolytic solutions of different pH and constant ionic strength 3.7 M ( $\text{H}_2\text{SO}_4 + \text{NaHSO}_4$ ), were employed. Solutions were made of Milli-Q purified water, NaOH (Carlo Erba, RPE-ACS) and  $\text{H}_2\text{SO}_4$  (Backer, p.a.). It is extremely important to keep the ionic strength constant because the physicochemical behaviour of polyelectrolytes is strongly affected by ionic screening [14,42]. The pH of these solutions was previously measured with a glass electrode adequate for acid media (Ross, Orion Research) by using a pH-meter (Cole-Palmer 59003-15). As a control, the pHs of several solutions were also measured using a Pd(Pd) hydrogen electrode [43].

As Pani films show the so-called “Electrochemically Induced Ageing” at reducing potentials [41,44], the electrodes were polarized at three potentials values in that range ( $-0.15$ ,  $-0.05$ , and  $0.05 \text{ V}$ ) during 20 min in 3.7-M  $\text{H}_2\text{SO}_4$  solution, to reduce and age the modified electrode before starting the spectrophotometric determination.

The proton dissociation curve was performed starting with the spectrum of the Pani film in the 3.7-M  $\text{H}_2\text{SO}_4$  solution. Then, this solution was replaced sequentially by solutions of different pH and constant ionic strength equal to 3.7-M obtained by mixing  $\text{H}_2\text{SO}_4$  and  $\text{NaHSO}_4$  solutions. The potential of the cell was opened

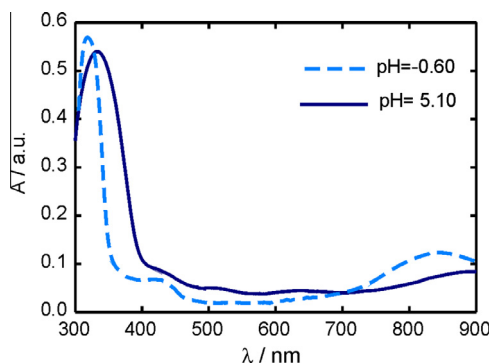


Fig. 1. Pani spectra at the two extreme pH values.  $E = -0.15 \text{ V}$ .

**Table 1**  
Values of  $pK_{a,LE}$  and  $pK_{a,E}$  reported in the literature.

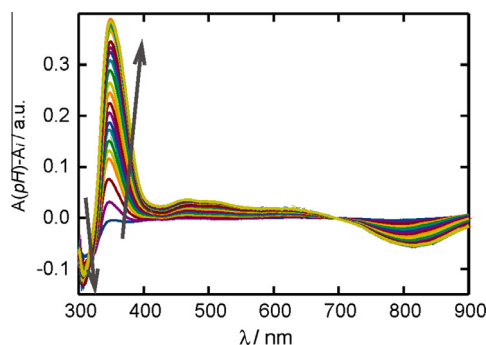
$pK_{a,LE}$	$pK_{a,E}$	Method
–	$\approx 3$	DC conductivity of pellets of Pani chemically synthesized in different pH media [20,21]
2.5	6.5	Acid–base titrations of aqueous dispersions of Pani [19]
–	$\approx 3$	Mass changes (EQMB) in different pH media [22]
2.5	5.5	Acid–base titrations of aqueous dispersions of Pani [23]
–	$\approx 3$	Theoretical study of Ref. [20] data. Apparent $pK_a$ values are informed [24]
$\approx 1.5$	$\approx 4.8$	Theoretical model applied to data of Ref. [23]. Interactions between binding sites are considered and intrinsic constants are fitted [25]
–	$\approx 3$	UV–visible spectra changes of Pani films in different pH media [26]
–	$\approx 7$	Absorbance changes of Pani films in buffers phosphate-citrate [27]
–	5.8	Acid–base titrations of aqueous dispersions of Pani in different pH and ionic strength. A binding distribution dependent on the ionic strength is recognized [28]
–	$\approx 5.5$	FTIR-ATR measurements of counterions [29]
–	7.4	UV–visible spectra changes of Pani and other derivatives films in different pH buffers [30]
–	4–8.3	UV–visible spectra changes of Pani synthesized in several conditions in different pH buffers. Fractional exponents and apparent constants are determined [31]
–	7.5–8.6	UV–visible spectra changes of Pani synthesized in several conditions in different pH buffers. Fractional exponents and apparent constants are determined [32]
–	0.17	Study of transport of protons and Fe(III) across Pani membranes [33]
–	3.5, 5.4	UV–visible spectra changes of Pani synthesized in several conditions in different pH buffers. Fractional exponents and apparent constants are determined [34]
–	4.4	UV–visible spectra changes of Pani nanoparticles dispersions in different pH media. Fractional exponents and apparent constants are determined [35]
–	6.8	UV–visible spectra changes of electrochemically synthesized Pani films [36]
–	4.4	UV–visible spectra changes of Pani nanoparticles [10]
–	6.7	UV–visible spectra changes of chemically synthesized Pani films [37]
–	5.4	Amperometric determination of zero current potential [7]
–	$\approx 2$	Monte-Carlo Simulations [38]

just the time (<10 s) required to exchange the solutions by employing syringes. After each change of solution, and before to carry out the spectrophotometric measurement, it was waited 5 min to reach the ionic equilibrium between the film and the electrolyte, at each one of the potentials studied. After this waiting time, no additional spectral changes were observed.

### 3. Results

The absorption spectra of Pani film, recorded in two different pH solutions are shown in Fig. 1. It is observed that the main feature, at 360 nm, decreases in intensity and shifts to longer wavelengths as the solution pH increases. This fact must be a consequence of the deprotonation of the amine groups [45,46]. In Fig. 2 it is shown the difference spectra of the Pani film, measured at  $E = -0.15$  V. These are the difference between the absorbance at a particular pH value, minus the absorbance at  $pH = -0.6$ ,  $A_i$ .

The analytical wavelength was chosen as that at which the absorbance variations are the greatest, that is  $\lambda = 360$  nm.



**Fig. 2.** Difference spectra of a Pani film at several pH values,  $A(pH)$ , with respect to that corresponding to  $pH = -0.6$ ,  $A_i$ . Arrows indicate increasing pH values in the range,  $-0.6 \leq pH \leq 5.10$ .  $E = -0.15$  V.

The relative change of absorbance of the band at 360 nm might be considered as a measure of the proton dissociation fraction,  $\alpha_R$ . So, it can be calculated as:

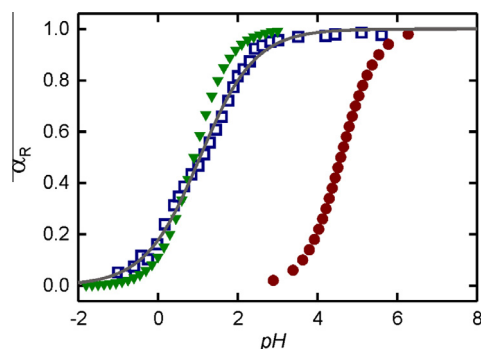
$$\alpha_R = \frac{A(pH) - A_i}{\Delta A_T} \quad (3)$$

where  $\Delta A_T$  is the total absorbance change between  $A(pH = 5.10)$  and  $A_i$ .

The resulting  $\alpha_R$  values are shown, as a function of pH, in Fig. 3. Also, and for the sake of comparison, the corresponding plots for two related simple substances, N,N-diphenylamine ( $pK_a = 0.9$ ) and aniline ( $pK_a = 4.58$ ) are shown. These two monomers are related to LE from the viewpoint of the acid–base behaviour [47]. The chemical structures of reduced polyaniline (LE), N,N-diphenylamine, and aniline are shown in Fig. 4.

In what follows the subscript LE will be dropped in the understanding that only this redox form is being considered.

In Fig. 3 it is observed that  $\alpha_R = 0.5$  at  $pH = 1.02$ . Also, it is also observed that the sigmoid curve for the polymer film extends over a wider pH range than those calculated for the monomers. This



**Fig. 3.** Dependence of the dissociation degree of Pani film on the electrolyte pH. Experimental values of Pani at  $\lambda = 360$  nm (squares) and results of the fit (continuous line).  $E = -0.15$  V. Calculated values for N,N-diphenylamine (triangles), and for aniline (circles).

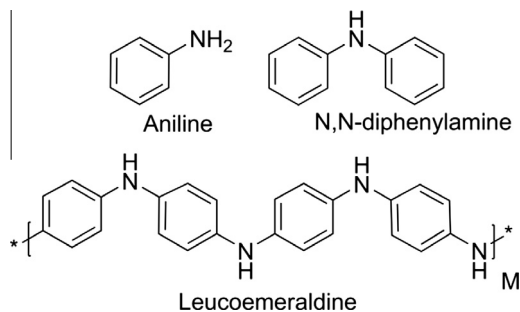


Fig. 4. Chemical structures of aniline, N,N-diphenylamine and leucoemeraldine (base form).

experimental fact is indicative of a distribution of dissociation constants in the polymer [14,15,42]. Also, it is interesting to point out that the  $pK_a$  of the LE seems to be closer to that of N,N-diphenylamine than to that of the aniline.

#### 4. Discussion

The reduced form of Pani shows important optical transitions only below 350 nm, and a very small band at 850 nm. The bands at  $\lambda < 300$  and 325 nm are due to the  $\pi \rightarrow \pi^*$  transitions, named B band of benzoid rings [48], distorted by amine groups protonated to different extents [48–50]. This transition, within the framework of these materials, is associated with the band-gap in the reduced state [45,51]. By protonation, the bathochromic effect of the amine group diminishes and the transition moves to shorter wavelengths as a consequence of the increase of the band-gap [45,46].

##### 4.1. Dissociation constant distribution in reduced polyaniline

As it was previously mentioned, being Pani a polyelectrolyte, its acid–base behaviour should be characterized by a distribution of dissociation constant values. The *apparent dissociation constant*,  $K_{a,app}$ , is defined by a Henderson–Hasselbalch type of equation, which for the acid dissociation reaction of the reduced form (reaction 1) is written as:

$$pK_{a,app} = pH - \log(\alpha_R / (1 - \alpha_R)) \quad (4)$$

For polyelectrolytes,  $pK_{a,app}$  depends on  $\alpha_R$ . The apparent acid dissociation constant includes the conformational changes that happen during the protonation (or deprotonation), the interaction between charged neighbour sites and also the effect of ionic strength due to the screening of them [14,42]. Usually, these effects are taken into account by introducing a dependence of the dissociation constant on the dissociation degree. This dissociation constant is usually referred to as  $pK_{a,app}(\alpha_R)$ .

After determining the  $pK_{a,app}(\alpha_R)$  from Eq. (4), the  $pK_{a,app}(\alpha_R)$  distribution curve may be obtained from a plot of  $\alpha_R$  as a function of  $pK_{a,app}(\alpha_R)$  (Fig. SI 5). It is interesting to remember that in the case of electrochemically active polymers, and in virtue of the coupling between proton binding and redox state [12], the  $pK_{a,app}(\alpha_R)$  in Eq. (4) should also be a function of the applied potential, experimental variable that in this work is kept controlled. The results obtained for other potentials,  $E = -0.05$  V and  $E = 0.05$  V, are presented in the Supplementary material (Fig. SI 3). Studies previously performed show that at these potentials the stable form is the reduced one [13]. Although the apparent formal redox potential is pH dependent, it is higher than 0.2 V vs. SCE (Fig. SI 4).

In the case of a simple substance, the dissociation degree as a function of  $pK_a$  is a step function. On the contrary, in the case of LE the graph is a sigmoid curve, which implies an apparent

dissociation constant distribution (Fig. SI 5). This is a characteristic of polyelectrolytes [14,42]. As it was mentioned above, in this type of substances, departures from the ideal behaviour come out from three mayor contributions: (i) conformational changes, as the fixed charges in the polymer increase (or decrease); (ii) interactions between the fixed charges, and (iii) changes in the electrostatic free energy of charging with the ionic strength of the electrolyte. Usually, this term depends on the square root of the ionic strength of the solution [14,16]. All these contributions depend on the fraction of protonated sites. Then, at high and constant ionic strength, and neglecting conformational changes, the departure of the ideal behaviour could be assigned to interactions between proton binding sites.

##### 4.2. A simple statistical thermodynamic model for proton binding

To account for interactions between neighbour sites of proton binding there are two simple choices: The unidimensional Ising model, or the Bragg–Williams approximation (*Mean Field Approximation*). The unidimensional Ising model can be solved exactly but it implies considering only interactions between neighbour sites in a single chain [52,53]. The Bragg–Williams approximation [53] has the disadvantage that it is assumed an homogeneous distribution of sites and predicts just a linear dependence of  $pK_{a,app}(\alpha_R)$  on  $\alpha_R$ . So, it will not adequately represent the experimental data for  $\alpha_R < 0.2$  and  $\alpha_R > 0.8$ . On the other hand, the unidimensional Ising model does not fit the present experimental results. That is the reason why in this work it will be discussed a simple statistical thermodynamic model, based on the mean field approximation.

It will be considered that the polymer is fully reduced. Therefore there will be only one kind of proton binding sites: that of the amine groups. The model could be extended to the case in which the polymer is not fully reduced, but that condition will not be considered in this work. The model is described in the Appendix A. Here, it will only be discussed the resulting expression for the binding constant.

$$pK_{a,app}(\alpha_R) = \left( pK_{a,int} + \frac{\Delta\epsilon_{R,m}}{2.303kT} \right) - \frac{\Delta\epsilon_{R,m}}{2.303kT} 2\alpha_R \quad (5)$$

where following the common usage, it is defined the *intrinsic* equilibrium constant  $pK_{a,int}$  as the part of  $pK_{a,app}$  independent of  $\alpha_R$  and  $\Delta\epsilon_{R,m} = w(2\epsilon_{01} - \epsilon_{00} - \epsilon_{11})/2$  is the change of the molar interaction energy per pair, for the reaction between a pair of two free sites with a pair of two occupied sites, to give two pairs of sites in which one of them is unoccupied and the other one is occupied, being  $w$  the number of neighbour sites. This reaction that can be represented as Eq. (6), where the subscript 1 denotes an occupied site, and 0 an empty site.

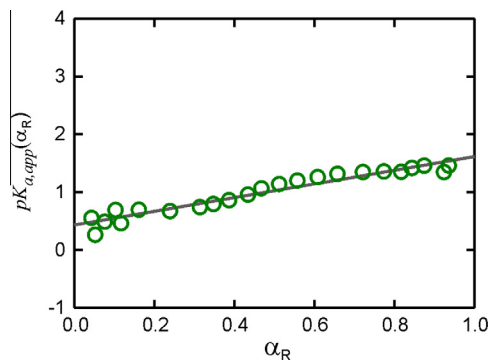


Fig. 5. Experimental values of  $pK_{a,app}(\alpha_R)$  vs.  $\alpha_R$ , applied potential  $E = -0.15$  V (○), and linear fit (—).





Being charged species, this interaction energy will be dependent on the salt concentration, which is constant for all the experiments. In Fig. 5, it is shown the plot of  $pK_{a,app}(\alpha_R)$  vs.  $\alpha_R$ , for  $E = -0.15$  V. Here,  $\Delta\epsilon_{R,m}$  can be determined from the slope of the graphic and  $pK_{a,int}$  from the ordinate at the origin. The results are summarized in Table 2 for the applied potentials (Fig. SI 6). The mean  $\Delta\epsilon_{R,m}$  value is  $-4.1 \pm 2.5$  kJ mol<sup>-1</sup>, and the  $pK_{a,int}$  results  $1.35 \pm 0.3$ .

#### 4.3. Comparison of the $pK_{a,int}$ with that of related monomers

Usually, the comparative acid–base behaviour of different monomers and dimers, of aromatic amines in this case, is done considering the basicity of the non protonated species on the basis of the corresponding  $K_b$  protonation constants. However, the point of view in this work is to study the dissociation of the corresponding protonated species.

When considering the  $K_b$  of dibasic molecules is usual to quote them as  $K_{b1}$  and  $K_{b2}$  for the first and second protonation reactions, respectively. However, it deserves to remember that  $K_{a1} = K_w/K_{b2}$  and  $K_{a2} = K_w/K_{b1}$  where  $K_{a1}$  and  $K_{a2}$  are the first and second acid dissociation constants, respectively, and  $K_w$  is the ionic product of water.

Comparing the acid–base behaviour of the monomers, aniline ( $pK_a = 4.58$ ) and N,N-diphenylamine ( $pK_a = 0.9$ ), it is interesting to observe that the binding of a second phenyl group to the nitrogen in the aniline, to yield N,N-diphenylamine, greatly decreases the  $pK_a$  of the first one [47]. In leucoemeraldine, phenylene groups are shared with two –NH– groups in *para* position. The effect of the substituent on the N atom is probably less intense than the effect of the phenyl group in N,N-diphenylamine and its  $pK_a$  value becomes higher than that of N,N-diphenylamine, but lower than that of the aniline. In other words, from this comparison it should be expected the  $pK_a$  value of the amine groups in reduced Pani to be between 0.9 and 4.58. This is an interesting point; the comparison between the acid–base properties of both monomers gives an indication of the type of departures that happen in going from the monomer to the polymer [14,42]. In Table 3 the  $pK_a$  values of aniline and its dimers are shown. These values were determined by Okamoto et al. employing a spectrophotometric method [31]. The chemical structures of the three dimers are shown in Fig. 6.

At this point, it is interesting to analyze the  $pK_a$  values of N-phenyl-*p*-phenylenediamine. The  $pK_{a,2}$  value corresponds to the terminal amine group (primary amine), as it can be deduced from its proximity to the  $pK_a$  of aniline. So, the presence of a N-phenylamine group (electron donor) in *para* position shifts the  $pK_a$  to higher values, as a consequence of the increase of the basicity of the terminal amine group. The  $pK_{a,1}$  value corresponds to the secondary amine group of N-phenyl-*p*-phenylenediamine. In this case, the comparison must be done with N,N-diphenylamine. As it can be seen in Table 3, now the presence of the substituents shifts the  $pK_a$  from 0.9 in N,N-diphenylamine to  $-0.1$  in N-phenyl-*p*-phenylenediamine. This seems to be contrary to the former explanation. However, the difference comes from the fact that when measuring the  $pK_{a,1}$  of N-phenyl-*p*-phenylenediamine, the terminal amine group is completely protonated, so an ammonium group (electron acceptor) must be considered.

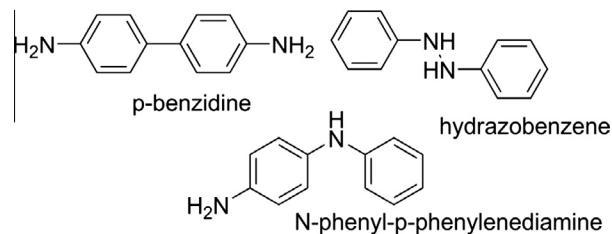
**Table 2**  
Values of  $\Delta\epsilon_{R,m}$  and  $pK_{a,int}$  determined by linear fitting.

E/V	$pK_{a,int}$	$\Delta\epsilon_{R,m}/\text{kJ mol}^{-1}$
-0.15	1.02	-3.3
-0.05	1.44	-6.8
0.05	1.60	-2.1

**Table 3**

$pK_a$  values of aniline and its dimers [31].  $pK_{a,1}$  and  $pK_{a,2}$  are the first and second dissociation constants, respectively.

Compound	$pK_{a,1}$	$pK_{a,2}$
Aniline	4.86	–
N,N-diphenylamine	0.9	–
N-phenyl- <i>p</i> -phenylenediamine	-0.1	5.72
Hydrazobenzene	<-1	4.22
<i>p</i> -Benzidine	3.57	4.66

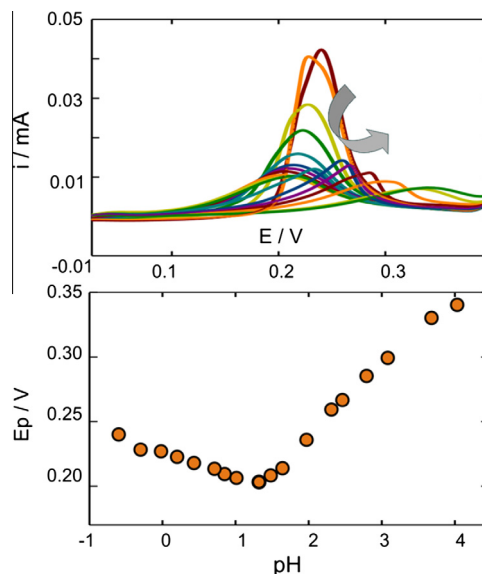


**Fig. 6.** Chemical structures of aniline dimers.

From this analysis, the situation in leucoemeraldine could be interpreted as follows. It will be considered a particular secondary amine group within the polymer. Initially, the presence of another N-phenylamine group in *para* position must increase the basicity of the group considered as it happens in the  $pK_{a,2}$  value of N-phenyl-*p*-phenylenediamine. However, as the polymer becomes protonated, N-phenylammonium groups must be considered, whose effect is opposite and decreases the basicity as it happens in the  $pK_{a,1}$  of N-phenyl-*p*-phenylenediamine. Beyond the specific effect, this allows concluding that the  $pK_{a,int}$  of amine groups in leucoemeraldine must depend on the degree of protonation, as it was discussed in the previous section.

#### 4.4. Consequences of proton binding in the pH dependence of the voltammetric peak potential

In view of the results reported above, preliminar measurements were performed to obtain information about the dependence of the



**Fig. 7.** Anodic voltammetric wave of a Pani covered ITO electrode in electrolyte solutions of different pH values, recorded at  $0.001$  V s<sup>-1</sup>. The arrow indicates increasing pH values (top). Voltammetric peak potentials as a function of pH (bottom).

voltammetric peak potential on the electrolyte pH. Fig. 7 shows the voltammetric response of a Pani modified electrode in electrolyte solutions of different pH values. As it is shown there, in the pH range between  $-0.6 < \text{pH} < 1.2$ , the peak potential value diminishes with a slope  $s_1 = -0.027$  V/decade as the pH increases. Then, the voltammetric peak potential moves in the opposite direction, with a slope of about  $s_2 = 0.061$  V/decade as the pH increases. In the case of CPs, the peak position is not only determined by the faradaic redox contribution but also by the capacitive one [53]. Nevertheless, a qualitative interpretation can be achieved from the analysis of just the experimental response (taking into account that the changes in the peak potential values, due to alterations of the capacitive response with the electrolyte pH, are expected to be small in comparison with those due to the faradaic contribution). Several authors have considered the peak potential shift with the electrolyte pH ( $\partial E_p/\partial \text{pH}$ ) an appropriate medium to get information about the redox mechanism in CPs [17,54–59].

In a previous work [13], it was proposed that the peak potential is affected by the pH not only due to the dependence of the electrochemical reaction on electrolyte pH (see Fig. SI.1) but also by the interaction between the charged redox centres and the proton binding on both the oxidized and reduced segments (see Figs. 8 and 9 in Ref. [13] for the pH dependence of those contributions). On the basis of these ideas it is possible to explain the results shown in Fig. 7.

In the pH range between  $-0.6 < \text{pH} < 1.2$ , both reduced and oxidized segments are fully protonated. Then, no net change of bound protons should be noted during the redox commutation; the protons produced by the oxidation reaction will protonate the imine segments. In this condition the slope  $\partial E_p/\partial \text{pH}$  should be  $-0.059$  V. However, this value differs from the slope experimentally obtained here. The difference can be attributed to effects of binding and interaction mentioned in the paragraph above, in that pH range (also, see Figs. 8 and 9 in Ref. [13]). Other authors have reported a value of  $\partial E_p/\partial \text{pH} = 0.059$  V for Pani films, in the range  $\text{pH} -2 < \text{pH} < 0.2$  [17,18]. However, these authors employed HCl solutions for which the interaction and binding effect should be different from that of the  $\text{H}_2\text{SO}_4 + \text{NaHSO}_4$  solutions.

As the pH increases, at  $\text{pH} \approx 1.3$ , the reduced segments start deprotonating ( $\text{p}K_{a,R}$  about 1) while the oxidized ones are still protonated ( $\text{p}K_{a,Ox} > 4$ ). At higher pH values, all the protons generated by the redox reaction are completely employed for protonation of oxidized segments and no extra protons are needed. This dependence has been also reported for Pani [17,18] in HCl solutions. In this pH range the pH dependence of the electron exchange reaction is compensated by the effect of interactions and proton binding effect. Also note that the polymer becomes charged and anions enter the polymer phase to maintain electroneutrality [29,60].

For  $1.5 < \text{pH} < 4.0$ , the influence of the interaction between the redox centres and protonation keeps increasing with pH so as to overcompensate the effect of the electrochemical reaction and the peak potential increases positively.

## 5. Conclusions

In this work it is studied the acid–base equilibrium of leucoemeraldine, and the results are analyzed by a simple statistical thermodynamic model. This model does well fit the linear relationship between the apparent  $\text{p}K_a$  and the dissociation degree in a range around  $\alpha_R = 0.5$ .

The resulting value of intrinsic  $\text{p}K_{a,int} \approx 1.35$  obtained in this study is smaller than those obtained by previous workers who performed their experiments without potential control. Moreover, the analysis and comparison of the  $\text{p}K_a$  values of monomers and dimers related to Pani in the reduced state, with the  $\text{p}K_{a,int}$  value obtained for the polymer are presented in favour of our results.

The experimental results indicate that there is a distribution of apparent dissociation constants rather than a single value. Being the Pani a polyelectrolyte, this is an expected conclusion. The  $\text{p}K_{a,app}$  distribution is related to the interactions between proton binding sites. The interactions are principally due to the existence of charged groups. As the coverage degree of the proton binding sites increases, the charged groups should be responsible for the decline of the proton affinity of the sites. The effect is a decrease of the apparent  $\text{p}K_{a,app}$  as the pH decreases. This effect is observed, in the analysis of the substitution effect in N,N-diphenylamine, which could be considered as the acid–base minimal unit of the completely reduced polymer.

Finally, the present results are in good agreement with our previous indirectly determined values, thus reinforcing the applicability of the simple statistical thermodynamic model for the coupling between redox potentials and proton binding in electroactive polymers [13].

## Conflict of interest

There is no conflict of interest.

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## Appendix A

It will be considered that the polymer is composed of intertwined chains. The chains have  $M$  segments, each of them have  $\chi$  sites for proton binding. So, the total number of proton binding sites is  $B = \chi M$ . The total number of bound protons is  $N$  [12].

It will be supposed that each proton binding site interacts with  $w$  neighbour sites, with constant interaction energy, proper of this each particular pair of sites.

The canonical partition function of the proton binding sites in the presence of interactions can be written as:

$$Q'_N(B, N, T) = \left[ \frac{B!}{(B-N)!N!} q_1^N q_0^{(B-N)} \right] \prod_p (\exp(-P_p \varepsilon_p / kT)) \quad (\text{A.1})$$

where  $q_1$  and  $q_0$  are the internal partition functions of the occupied and empty proton binding sites respectively when no interactions are considered [52,53]. The product on the right involves all the pairs of interacting neighbour sites and it introduces the interactions. There  $P_p$  is the number of total pair of interacting neighbour sites of the type  $p$  and  $\varepsilon_p$  is the corresponding interaction energy. Note that in the case of charged species, this interaction energy will be dependent on the salt concentration due to screening effects. It is also important to note that when all interaction energies are null, this last factor becomes the unity and the partition function does coincide with that of the Langmuir isotherm.

$$\prod_p (\exp(-\varepsilon_p / kT))^{P_p} = \exp(-\varepsilon_{11} P_{11} / kT) \exp(-\varepsilon_{01} P_{01} / kT) \times \exp(-\varepsilon_{00} P_{00} / kT) \quad (\text{A.2})$$

where 00, 11 and 01 mean the pair of binding sites with both sites empty, both sites occupied and just one of them occupied respectively. Within the Bragg–Williams approximation, the number of neighbour pairs can be calculated as

$$P_{00} = \frac{w(B-N)^2}{2B} \quad (\text{A.3})$$

$$P_{11} = \frac{w(N)^2}{2B} \quad (\text{A.4})$$

$$P_{01} = \frac{w(B-N)N}{B} \quad (\text{A.5})$$

Then,

$$Q'_N(B, N, T) = \frac{B!}{(B-N)!N!} (q_1^*)^N (q_0^*)^{(B-N)} \left( \exp\left(-\frac{\Delta\epsilon_{R,m}}{kT}\right) \right)^{N(B-N)/B} \quad (\text{A.6})$$

where  $q_1^* = q_1 \exp(-\frac{w\epsilon_{11}}{2kT})$  and  $q_0^* = q_0 \exp(-\frac{w\epsilon_{00}}{2kT})$  are the internal partition functions of occupied and empty interacting binding sites respectively and

$$\Delta\epsilon_{R,m} = \frac{1}{2} w(2\epsilon_{01} - \epsilon_{00} - \epsilon_{11}) \quad (\text{A.7})$$

In Ref. [13] it is explained that the basic thermodynamic equation for this system, considering an electrode reaction of the type  $Ox + \nu_H H^+ + \nu_e e^- \rightarrow R$  (as it is the case of Pani, Fig. SI 1), at constant temperature, can be written as [13]:

$$dA = (\bar{\mu}_{Ox} - \bar{\mu}_R + \nu_e \bar{\mu}_e + \nu_H \bar{\mu}_H) dn_{Ox} + (\mu_{N,Ox} - \mu_{N,R}) dN_{Ox} + \mu_{N,R} dN + (d\mu_p, Ox - d\mu_{p,R}) dM_{Ox} - d\mu_{p,R} dMR \quad (\text{A.8})$$

where  $A$  is the Helmholtz free energy;  $\bar{\mu}_{Ox}$ ,  $\bar{\mu}_R$ ,  $\bar{\mu}_e$  and  $\bar{\mu}_H$  are the electrochemical potential of oxidized and reduced redox centres, electrons and protons, respectively;  $\mu_{N,Ox}$  and  $\mu_{N,R}$  are the chemicals potentials of the proton bound sites of the oxidized and the reduced segments and  $\mu_{p,Ox}$  and  $\mu_{p,R}$  are the chemical potentials due to mixing and deformation of the oxidized and reduced polymer, respectively [11,12]. It can be shown that, under the assumptions made, these chemical potentials are independent of  $M$ , and then of  $n_{Ox}$  [11]. Therefore, these contributions add directly to the standard part of the redox potential as constant terms.

The Helmholtz free energy is related to the total partition function of the system,  $Q$ , by

$$A = -kT \ln Q \quad (\text{A.9})$$

This allows to obtain the chemical potential of the bound species on the reduced segments [52]. According to Eq. (A.8) and considering that all the redox centers are in its reduced form,

$$-\mu_{N,R}/kT = \left( \frac{\partial \ln Q}{\partial N} \right)_{B,T} \quad (\text{A.10})$$

The total partition function can be written as

$$Q = Q_n Q_H Q_M Q'_N \quad (\text{A.11})$$

where  $Q_M$  is the partition function of the segments,  $Q'_N$  is the partition function of the bound species,  $Q_n$  is the partition function of the redox centres and  $Q_H$  is the partition function of protons in solution. Detailed expressions for  $Q_M$ ,  $Q_n$  and  $Q_H$  are given in Ref. [13]. They do not depend on  $N$ . So, Eq. (A.10) can be written as

$$\mu_{N,R} = -kT \left( \frac{\partial \ln Q'_N}{\partial N} \right)_{B,T} \quad (\text{A.12})$$

Taking into account expression (A.6) for the partition function,

$$\left( \frac{\partial \ln Q'_N}{\partial N} \right)_{T,B} = \ln \left( \frac{B-N}{N} \frac{q_1^*}{q_0^*} \right) - \left( 1 - 2 \frac{N}{B} \right) \frac{\Delta\epsilon_{R,m}}{kT} \quad (\text{A.13})$$

By defining the dissociation degree as  $\alpha_R = (B-N)/B$ , it results

$$\left( \frac{\partial \ln Q'_N}{\partial N} \right)_{T,B} = \ln \left( \frac{\alpha_R}{1-\alpha_R} \frac{q_1^*}{q_0^*} \right) + (1-2\alpha_R) \frac{\Delta\epsilon_{R,m}}{kT} \quad (\text{A.14})$$

### A.1. The dissociation acid constant

By considering the acid–base equilibrium of the reduced segments



where  $RH^+$  means an occupied proton binding site, whose chemical potential is  $\mu_{N,R}$  and  $R^*$  means an empty proton binding site whose chemical potential is  $\mu_{R^*}$ . In equilibrium,

$$\mu_{N,R} = \mu_{R^*} + \mu_H^0 + kT \ln a_H \quad (\text{A.16})$$

By using the expression for  $\mu_{N,R}$  from Eq. (A.14), and considering the standard chemical potential of protons in solution to be zero by convention [61], it results

$$-\ln \left( a_H \frac{\alpha_R}{1-\alpha_R} \right) = \frac{\mu_{R^*}}{kT} + \ln \left( \frac{q_1^*}{q_0^*} \right) + (1-2\alpha_R) \frac{\Delta\epsilon_{R,m}}{kT} \quad (\text{A.17})$$

By employing the definition of the apparent dissociation constant given in Eq. (4), it results

$$K_{a,app} = \frac{\alpha_R a_H}{1-\alpha_R} \quad (\text{A.18})$$

So that

$$K_{a,app} = \left( \frac{q_0^*}{q_1^*} \right) \exp \left( -\frac{\mu_{R^*}}{kT} \right) \exp \left[ (2\alpha_R - 1) \frac{\Delta\epsilon_{R,m}}{kT} \right] \quad (\text{A.19})$$

$pK_{a,int}$  is defined as the equilibrium constant in the absence of interactions.

$$K_{a,int} = \left( \frac{q_0^*}{q_1^*} \right) \exp \left( -\frac{\mu_{R^*}}{kT} \right) \quad (\text{A.20})$$

So,  $pK_{a,app}(\alpha_R)$  results

$$pK_{a,app}(\alpha_R) = \left( pK_{a,int} + \frac{\Delta\epsilon_{R,m}}{2.303kT} \right) - \frac{\Delta\epsilon_{R,m}}{2.303kT} 2\alpha_R \quad (5)$$

It is interesting to note that within this model,  $pK_{a,int}$  does coincide with the  $pK_a$  value at hemi-protonation,  $pK_{a,app}(\alpha_R = 0.5) = pK_{a,int}$ .

## Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jelechem.2014.03.003>.

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